Direct Assembly of Modified Proteins on Carbon Nanotubes in an Aqueous Solution

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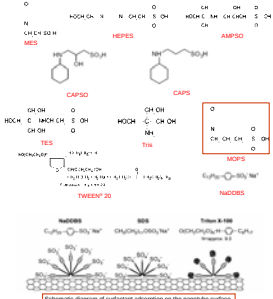
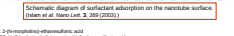
ABSTRACT

Carbon nanotubes (CNTs) have superior mechanical and electrical properties that have opened up many potential applications. However, poor dispersibility and solubility, due to the substantial van der Waals attraction between tubes, have prevented the use of CNTs in practical applications, especially biotechnology applications. Effective dispersion of CNTs into small bundles or individual tubes in solvents is crucial to ensure homogeneous properties and enable practical applications. In addition to dispersion of CNTs into a solvent, the selection of appropriate solvent, which is compatible with a desired matrix, is an important factor to improve the mechanical, thermal, optical, and electrical properties of CNT-based fibers and composites. In particular, dispersion of CNTs into an aqueous system has been a challenge due to the hydrophobic nature of CNTs. Here we show an effective method for dispersion of both single wall CNTs (SWCNTs) and few wall CNTs (FWCNTs) in an aqueous buffer solution. We also show an assembly of cationized Pt-cored ferritins on the well dispersed CNTs in an aqueous buffer solution.

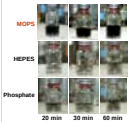
Buffers Studied



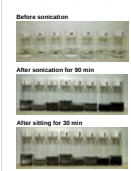


Schematic diagram of surfactant adsorption on the nanotube surface. (Islam *et al. Nano Lett.* **3**, 269 (2002)).

MES: 2-(N-morpholino)-ethanesulfonic acid
HEPES: N-(2-hydroxyethyl)piperazine-N'-2-ethanesulfonic acid
AMPSO: N-(1,1-dimethyl-2-hydroxyethyl)-3-amino-2-hydroxypropanesulfonic acid
CAPSO: 3-(cyclohexylamino)-2-hydroxy-1-propanesulfonic acid
CAPS: N-(cyclohexyl)-3-aminopropanesulfonic acid
TES: N-Tris(hydroxymethyl)-2-aminoethanesulfonic acid
Tris: Trishydroxymethylaminomethane
MOPS: 3-(N-morpholino)-propanesulfonic acid
TWEEN 20: Polyoxyethylenesorbitan monolaurate
NaDDBS: Sodium dodecylbenzene sulfonate



Photos of initial HiPCO SWCNTS dispersion in the various buffers: MOPS (0.05 M (1.05 wt. %) with 0.025 M NaCl (0.15 wt. %), pH 7.5) solution containing SWCNT at 0.125 mg/mL; HEPES (0.025 M (0.6 wt. %) with 0.025 M NaCl (0.15 wt. %), pH 7.3) solution containing SWCNT at 0.025 mg/mL and phosphate (0.05 M (0.8 wt. %) with 0.07 M NaCl (0.41 wt. %), pH 7.2) containing SWCNT at 0.05 mg/mL. All samples were pictured after sonication for 20, 30, and 60 min. Third pictures at each solution were taken after 30 min sonication and then adding 2 ml buffer more with 30 min sonication.

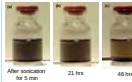


Photos of initial SW_{NT} SWCNT (0.5 mg/ml)-buffer suspensions after sonication for 90 min with:
(1) MES (0.1 M (2.0 wt. %) with 0.05 M NaCl (0.9 wt. %), pH 4.7),
(2) HEPES (0.05 M (1.2 wt. %) with 0.05 M NaCl (0.29 wt. %), pH 7.3),
(3) phosphate (0.1 M (1.6 wt. %) with 0.15 M NaCl (0.9 wt. %), pH 7.2),
(4) Tris (0.025 M (0.3 wt. %) with 0.05 M NaCl (0.29 wt. %), pH 7.5),
(5) CAPSO (0.1 M (2.4 wt. %) with 0.05 M NaCl (0.29 wt. %), pH 9.0),
(6) AMPSO (0.1 M (2.3 wt. %) with 0.05 M NaCl (0.29 wt. %), pH 9.0), and
(7) MOPS (0.1 M (2.1 wt. %) with 0.05 M NaCl (0.29 wt. %), pH 7.5).
(8) The solution contains SW_{NT} SWCNT of 1 mg/ml in MOPS (0.1 M (2.1 wt. %) without NaCl, pH 7.5) buffer.
All pictures are taken at initial dispersion state before and after sonication for 90 min and then after sitting for 30 min.

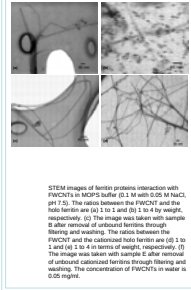
Ferritin Protein
- Iron storage protein in biological mechanisms in human, animal, and even bacteria.
- Contains up to ~4500 Fe^{3+} atoms.
- Stable and robust structure to withstand biologically extremes of high temperature (up to 80 °C) and pH variations (2.0-10.0).
- Hydrophilic and hydrophobic channels

Core materials:
- Natural (Ferrihydrite, $5Fe_2O_3 \cdot 9H_2O$)
- Magnetite-maghemite (Fe_3O_4-γ-Fe_2O_3)
- Trimethylamine-N-oxide (Me_3NO)
- Co, Mn, Ni, Cr, CoPt, Pt, Ru, Rh-W, etc
- CdS, CdSe (semiconductor QDs)
- Prussian Blue

STEM image of chemically prepared Pt-cored ferritins. STEM image was taken after addition of 200 $PtCl_4^{2-}$ into an apoferritin for 30 min and then reduction with $NaBH_4$ for 10 min.

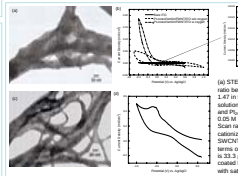


Photos of HiPCO SWCNT-MOPS dispersion solution containing 0.1 ml of calcinized holo ferritin at 10 mg/ml. The dispersion solution consists of 0.1 ml MOPS buffer without NaCl at pH 7.5 and HiPCO SWCNT of 0.1 mg/ml. Total volumes of SWNT dispersion solution is 7 ml. The ratio between the SWCNT and the Fe inside ferritin is 1 to 0.71 as a weight. The amount of Fe loading into the solution is 253.9 μg.



STEM images of ferritin protein interaction with FWCNTs in surfactant assisted suspensions: (a) holo ferritin and (b) calcinized holo ferritin affinity for TWEEN 20 assisted FWCNTs suspension, and (c) holo ferritin and (d) calcinized holo ferritin affinity for NaDDBS assisted FWNT suspension. The concentration of FWCNTs in water is 0.05 mg/ml and the ratio among the FWCNT, the ferritin, and the surfactant is 1 : 4 : 10 in terms of weight.

STEM images of ferritin proteins interaction with FWCNTs in MOPS buffer (0.1 M with 0.05 M NaCl, pH 7.5). The ratios between the FWCNT and the holo ferritin are (a) 1 to 1 and (b) 1 to 4 by weight, respectively. (c) The image was taken with sample B after removal of unbound ferritins through filtering and washing. The ratios between the FWCNT and the calcinized holo ferritin are (d) 1 to 1 and (e) 1 to 4 in terms of weight, respectively. (f) The image was taken with sample E after removal of unbound calcinized ferritins through filtering and washing. The concentration of FWCNTs in water is 0.05 mg/ml.



(a) STEM image of Pt_{cal}-cored ferritins on FWCNTs. The ratio between the FWCNT and the Pt-cored ferritin is 1 to 1.47 in terms of weight. The total Pt loading amount into the solution is 44.3 μg. (b) Cyclic voltammmograms of bare ITO, and Pt_{cal}-cored ferritins-FWCNT coated ITO electrode in 0.05 M phosphate buffer at pH 7.5 withwithout oxygen. Scan rate is 10 mV/s. (c) STEM image of Pt_{cal}- cored cationized ferritins on SWCNTs. The ratio between the SWCNT and the Pt-cored cationized ferritin is 1 to 0.4 in terms of weight. The total Pt loading amount into the solution is 33.3 μg. (d) CV of Pt_{cal}-cored cationized ferritin-SWCNT coated ITO electrode in 0.05 M phosphate buffer at pH 7.5 with saturated oxygen. Scan rate is 10 mV/s.

Ferritin protein-assembled SWCNT electrode

Summary

We demonstrated high performance electrodes for oxygen reduction using CNTs conjugated with uniformly populated platinum nanoparticles generated by the reconstitution of ferritin proteins. These electrodes were achieved by effectively dispersing CNTs into the aqueous MOPS buffer containing Pt-cored cationized ferritins. The nanosized Pt-cored ferritins on the CNTs displayed good catalytic activity for the electrochemical reduction of oxygen which is applicable to biofuel cell and fuel cell applications.

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